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(54) Title: POLYMERISATION PROCESS

(57) Abstract

The present invention relates to a start-up process of a continuous gas fluidised bed process for the polymerisation of olefin monomer selected from (a) ethylene, (b) propylene, (c) mixtures of ethylene and propylene, and (d) one or more other alpha-olefins mixed with (a), (b) or (c), in a fluidised bed reactor by continuously recycling a gaseous stream comprising at least some of the ethylene and/or propylene through a fluidised bed in said reactor in the presence of a polymerisation catalyst under reactive conditions, cooling at least part of said gaseous stream withdrawn from said reactor to a temperature at which liquid condenses out, separating at least part of the condensed liquid from the gaseous stream, and introducing at least part of the separated liquid directly into the fluidised bed using a liquid injection means, characterised in that at least part of the gaseous recycle stream by-passes the hereabove cooling/condensing/separating steps, and is reintroduced as the recycling gaseous stream passing through the reactor.

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POLYMERISATION PROCESS

The present invention relates to a continuous process for the gas-phase polymerisation of olefins in a fluidised bed reactor having improved levels of productivity and in particular to a start-up procedure for said process.

Processes for the homopolymerisation and copolymerisation of olefins in
5　the gas phase are well known in the art. Such processes can be conducted for example by introducing the gaseous monomer into a stirred and/or fluidised bed comprising polyolefin and a catalyst for the polymerisation.

In the fluidised bed polymerisation of olefins, the polymerisation is conducted in a fluidised bed reactor wherein a bed of polymer particles is
10　maintained in a fluidised state by means of an ascending gas stream comprising the gaseous reaction monomer. The start-up of such a polymerisation generally employs a bed of polymer particles similar to the polymer which it is desired to manufacture. During the course of polymerisation, fresh polymer is generated by the catalytic polymerisation of the monomer, and polymer product is withdrawn to
15　maintain the bed at more or less constant volume. An industrially favoured process employs a fluidisation grid to distribute the fluidising gas to the bed, and to act as a support for the bed when the supply of gas is cut off. The polymer produced is generally withdrawn from the reactor via a discharge conduit arranged in the lower portion of the reactor, near the fluidisation grid. The fluidised bed comprises a bed
20　of growing polymer particles, polymer product particles and catalyst particles. This bed is maintained in a fluidised condition by the continuous upward flow from the base of the reactor of a fluidising gas which comprises recycle gas from the top of the reactor together with make-up feed. The fluidising gas enters the bottom of the reactor and is passed, preferably through a fluidisation grid, to the fluidised
25　bed.

The polymerisation of olefins is an exothermic reaction and it is therefore necessary to provide means to cool the bed to remove the heat of polymerisation. In the absence of such cooling the bed would increase in temperature until, for example, the catalyst became inactive or the bed commenced to fuse. In the

5   fluidised bed polymerisation of olefins, the preferred method for removing the heat of polymerisation is by supplying to the polymerisation reactor a gas, the fluidising gas, which is at a temperature lower than the desired polymerisation temperature, passing the gas through the fluidised bed to conduct away the heat of polymerisation, removing the gas from the reactor and cooling it by passage

10   through an external heat exchanger, and recycling it to the bed. The temperature of the recycle gas can be adjusted in the heat exchanger to maintain the fluidised bed at the desired polymerisation temperature. In this method of polymerising alpha olefins, the recycle gas generally comprises the monomeric olefin, optionally together with, for example, an inert diluent gas such as nitrogen and/or a gaseous

15   chain transfer agent such as hydrogen. Thus the recycle gas serves to supply the monomer to the bed, to fluidise the bed, and to maintain the bed at the desired temperature. Monomers consumed by the polymerisation reaction are normally replaced by adding make up gas to the recycle gas stream.

It is well known that the production rate (i.e. the space time yield in terms

20   of weight of polymer produced per unit volume of reactor space per unit time) in commercial gas fluidised bed reactors of the afore-mentioned type is restricted by the maximum rate at which heat can be removed from the reactor. The rate of heat removal can be increased for example, by increasing the velocity of the recycle gas and/or reducing the temperature of the recycle gas and/or changing the heat

25   capacity of the recycle gas. However, there is a limit to the velocity of the recycle gas which can be used in commercial practice. Beyond this limit the bed can become unstable or even lift out of the reactor in the gas stream, leading to blockage of the recycle line and damage to the recycle gas compressor or blower. There is also a limit on the extent to which the recycle gas can be cooled in

30   practice. This is primarily determined by economic considerations, and in practise is normally determined by the temperature of the industrial cooling water available on site. Refrigeration can be employed if desired, but this adds to the production costs. Thus, in commercial practice, the use of cooled recycle gas as the sole means of removing the heat of polymerisation from the gas fluidised bed

35   polymerisation of olefins has the disadvantage of limiting the maximum production

rates obtainable.

The prior art suggests a number of methods for increasing the heat removal capacity of the recycle stream.

EP 89691 relates to a process for increasing the space time yield in continuous gas fluidised bed processes for the polymerisation of fluid monomers, the process comprising cooling part or all of the unreacted fluids to form a two phase mixture of gas and entrained liquid below the dew point and reintroducing said two phase mixture into the reactor. The specification of EP 89691 states that a primary limitation on the extent to which the recycle gas stream can be cooled below the dew point is in the requirement that the gas-to-liquid ratio be maintained at a level sufficient to keep the liquid phase of the two phase fluid mixture in an entrained or suspended condition until the liquid is vaporised, and further states that the quantity of liquid in the gas phase should not exceed about 20 weight percent, and preferably should not exceed about 10 weight percent, provided always that the velocity of the two phase recycle stream is high enough to keep the liquid phase in suspension in the gas and to support the fluidised bed within the reactor. EP 89691 further discloses that it is possible to form a two-phase fluid stream within the reactor at the point of injection by separately injecting gas and liquid under conditions which will produce a two phase stream, but that there is little advantage seen in operating in this fashion due to the added and unnecessary burden and cost of separating the gas and liquid phases after cooling.

EP 173261 relates to a particular means for introducing a recycle stream into fluidised bed reactors and, in particular, to a means for introducing a recycle stream comprising a two phase mixture of gas and entrained liquid as described in EP 89691 (supra).

WO 94/25495 describes a fluidised bed polymerisation process comprising passing a gaseous stream comprising monomer through a fluidised bed reactor in the presence of a catalyst under reactive conditions to produce polymeric product and a stream comprising unreacted monomer gases, compressing and cooling said stream, mixing said stream with feed components and returning a gas and liquid phase to said reactor, a method of determining stable operating conditions which comprises: (a) observing fluidised bulk density changes in the reactor associated with changes in the composition of the fluidising medium; and (b) increasing the cooling capacity of the recycle stream by changing the composition without exceeding the level at which a reduction in the fluidised bulk density or a parameter

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indicative thereof becomes irreversible.

US 5,436,304 relates to a process for polymerising alpha-olefin(s) in a gas phase reactor having a fluidised bed and a fluidising medium wherein the fluidising medium serves to control the cooling capacity of the reactor and wherein the bulk
5   density function (Z) is maintained at a value equal to or greater than the calculated limit of the bulk density function.

WO 94/28032, the contents of which are hereby incorporated by reference, relates to a continuous gas fluidised bed process in which the recycle gas stream is cooled to a temperature sufficient to form a liquid and a gas. By separating the
10   liquid from the gas and then feeding the liquid directly into the fluidised bed at or above the point at which the gaseous stream passing through the fluidised bed has substantially reached the temperature of the gaseous stream being withdrawn from the reactor, the total amount of liquid which may be reintroduced into the fluidised bed polymerisation reactor for the purpose of cooling the bed by evaporation of the
15   liquid can be increased thereby enhancing the level of cooling to achieve higher levels of productivity.

The separated liquid may be suitably injected into the fluidised bed by means of one or more nozzles arranged therein. The nozzles may be either gas-atomising nozzles in which an atomising gas is used to assist in the injection of
20   liquid or they may be liquid only spray type nozzles. When using the liquid only nozzles the turn down capability may be limited and it may be difficult to control the quantity of liquid which may be introduced into the fluidised bed. During start-up procedures for example it may be necessary to inject large quantities of liquid into the bed and these may have a detrimental effect on the operation of the
25   process in that the reaction may be quenched and the temperature of the reactor may be difficult to control. The injection of large quantities of liquid may indeed have an adverse effect on the composition of the fluidised bed thereby influencing the product.

As disclosed in WO 94/28032, a major concern regarding the introduction
30   of the separated liquid inside the fluidised bed is not to adversely affect the fluidisation of the bed or the quality of the product. In this way it would be advantageous to begin with the introduction of the separated liquid into the fluidised bed at the early stage of the polymerisation, i.e. at lower production rates.

We have now found that by providing the recycle gas stream line with a by-
35   pass of the cooling/condensing/separating steps, it is possible to early condense

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part of the recycle gas stream and introduce said condensed liquid into the fluidised bed at low production rate. The control of the reaction is thereby more easily maintained in steady state during the start-up of the process and the amount of liquid entering the fluidised bed is more easily controlled. .

5   Thus, according to the present invention there is provided a start-up process of a continuous gas fluidised bed process for the polymerisation of olefin monomer selected from (a) ethylene, (b) propylene, (c) mixtures of ethylene and propylene, and (d) one or more other alpha-olefins mixed with (a), (b) or (c), in a fluidised bed reactor by continuously recycling a gaseous stream comprising at

10   least some of the ethylene and/or propylene through a fluidised bed in said reactor in the presence of a polymerisation catalyst under reactive conditions, cooling at least part of said gaseous stream withdrawn from said reactor to a temperature at which liquid condenses out, separating at least part of the condensed liquid from the gaseous stream, and introducing at least part of the separated liquid directly

15   into the fluidised bed using a liquid injection means,
characterised in that at least part of the gaseous recycle stream by-passes the hereabove cooling/condensing/separating steps, and is reintroduced as the recycling by-pass gaseous stream passing through the reactor.

        Preferably, the by-pass gaseous stream is reintroduced in the reactor below

20   the bed together with the cold gaseous recycle stream coming from the separator.

        According to a preferred embodiment of the present invention, the by-pass gaseous stream is cooled to a temperature above which liquid condenses out before reintroduction in the reactor. A heat exchanger may suitably be used to cool said by-pass gaseous stream. Said heat exchanger used to cool the by-pass gaseous

25   stream to a temperature above which liquid condenses (or to above the dew point) may be called the « non-condensing exchanger ». Operating according to this embodiment allows the process to satisfy both the heat and mass balances. When the injection of the liquid is initiated, the « non-condensing » heat exchanger reduces it cooling requirements to accommodate the increase in cooling resulting

30   from the injection of liquid thereby maintaining the heat balance in the process. The quantity of liquid condensed by the « condensing » heat exchanger is equivalent to the amount of liquid injected into the fluidised bed which also aids the mass balance requirements of the process.

        Preferably the liquid coming from the separator is introduced directly into

35   the fluidised bed above the upper limit of the temperature gradient between the

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entering fluidising gas (the gaseous stream fed to the reactor) and the remainder of
the bed.

According to the present invention the amount of liquid directly injected
into the fluidised bed may be controlled by regulating the proportion of the gaseous
5   stream which is cooled to form the two phase mixture.

By use of the process according to the present invention the reaction
control is maintained in steady state. Also start-up of the injection of liquid may be
carried out at low plant throughput and switchover from conventional operation
can be carried out at low capacities when the fluidised bed is not very active.

10   Although the process of the present invention is directed to start-up
operation, the use of the by-pass may also be suitable for the continuous
polymerisation process as a control on the amount of liquid injected into the
fluidised bed as well as a control of the gas temperature . The amount of gaseous
recycle stream passing through the by-pass is preferably regulated by an automatic
15   valve as indicated in the accompanying drawings.

The minimal amount of gaseous recycle stream passing through the by-pass
during the start-up procedure represents preferably at least 5% of the total gaseous
recycle stream, more preferably at least 10 %. Although there is no upper limit for
this by-pass amount, it is preferred to limit it to 60 %, preferably to 50 %.

20   The better reaction control during the start-up procedure is not the only
advantage provided by the present invention. Indeed, the Applicants have also
found that the flexibility and the short time response provided by the start-up
process of the present invention allows a better temperature control of the
reaction ; it is now possible to work closer to the thermal exchange limits, i.e. at
25   superior production rates.

The gaseous recycle stream withdrawn from the reactor generally
comprises unreacted gaseous monomer(s), and optionally, inert hydrocarbon(s),
inert gases such as nitrogen. reaction activator(s) or moderator(s) such as
hydrogen as well as entrained catalyst and/or polymer particles (hereafter referred
30   to as "fines"). The gaseous recycle stream fed to the reactor additionally comprises
sufficient make-up monomers to replace those monomers polymerised in the
reactor.

The process according to the present invention is suitable for the
manufacture of polyolefins in the gas phase by the polymerisation of one or more
35   olefins at least one of which is ethylene or propylene. Preferred alpha-olefins for

use in the process of the present invention are those having from 3 to 8 carbon atoms. However, small quantities of alpha olefins having more than 8 carbon atoms, for example 9 to 18 carbon atoms, can be employed if desired. Thus, it is possible to produce homopolymers of ethylene or propylene or copolymers of

5   ethylene or propylene with one or more C_3-C_8 alpha-olefins. The preferred alpha-olefins are but-1-ene, pent-1-ene, hex-1-ene, 4-methylpent-1-ene, oct-1-ene and butadiene. Examples of higher olefins that can be copolymerised with the primary ethylene or propylene monomer, or as partial replacement for the C_3-C_8 alpha-olefin comonomer are dec-1-ene and ethylidene norbornene.

10   When the process is used for the copolymerisation of ethylene or propylene with alpha-olefins the ethylene or propylene is present as the major component of the monomers, and preferably is present in an amount at least 70%, more preferably at least 80% of the total monomers/comonomers.

The process according to the present invention may be used to prepare a

15   wide variety of polymer products for example linear low density polyethylene (LLDPE) based on copolymers of ethylene with but-1-ene, 4-methylpent-1-ene or hex-1-ene and high density polyethylene (HDPE) which can be for example, homopolyethylene or copolymers of ethylene with a small portion of higher alpha olefin, for example, but-1-ene, pent-1-ene, hex-1-ene or 4-methylpent-1-ene.

20   The liquid which condenses out of the gaseous recycle stream can be a condensable monomer, e.g. but-1-ene, hex-1-ene, octene used as a comonomer for the production of LLDPE or may be an inert condensable liquid, e.g. inert hydrocarbon(s), such as C_4-C_8 alkane(s) or cycloalkane(s), particularly butane, pentane or hexane.

25   It is important that the liquid should vaporise within the bed under the polymerisation conditions being employed so that the desired cooling effect is obtained and to avoid substantial accumulation of liquid within the bed. Suitably at least 95, preferably at least 98 weight percent and most preferably substantially all of the liquid fed to the bed evaporates therein. In the case of liquid comonomers,

30   some of the comonomer polymerises in the bed, and such polymerisation can be from the liquid and the gas phase. Associated olefin monomer can readily be tolerated within the bed provided that the quantities do not adversely affect the fluidisation characteristics of the bed.

The process is particularly suitable for polymerising olefins at an absolute

35   pressure of between 0.5 and 6 MPa and at a temperature of between 30°C and 130

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°C. For example for LLDPE production the temperature is suitably in the range
75-90°C and for HDPE the temperature is typically 80-105°C depending on the
activity of the catalyst used.

The polymerisation reaction may be carried out in the presence of a catalyst
5   system of the Ziegler-Natta type, consisting of a solid catalyst essentially
comprising a compound of a transition metal and of a cocatalyst comprising an
organic compound of a metal (i.e. an organometallic compound, for example an
alkylaluminium compound). High-activity catalyst systems have already been
known for a number of years and are capable of producing large quantities of
10   polymer in a relatively short time, and thus make it possible to avoid a step of
removing catalyst residues from the polymer. These high-activity catalyst systems
generally comprise a solid catalyst consisting essentially of atoms of transition
metal, of magnesium and of halogen. It is also possible to use a high-activity
catalyst consisting essentially of a chromium oxide activated by a heat treatment
15   and associated with a granular support based on a refractory oxide. The process is
also suitable for use with metallocene catalysts and Ziegler catalysts supported on
silica.

The catalyst may suitably be employed in the form of a prepolymer powder
prepared beforehand during a prepolymerisation stage with the aid of a catalyst as
20   described above. The prepolymerisation may be carried out by any suitable
process, for example, polymerisation in a liquid hydrocarbon diluent or in the gas
phase using a batch process, a semi-continuous process or a continuous process.

At least part of the gaseous recycle stream is thus cooled by means of a
heat exchanger or exchangers to a temperature such that liquid is condensed in the
25   gaseous recycle stream. Suitable heat exchangers are well known in the art.

The gaseous recycle stream leaving the top of the reactor has entrained
therein a quantity of catalyst and/or polymer particles and the majority of these may
be removed from the gaseous recycle stream by means of a cyclone. A small
proportion of these particles remain entrained in the gaseous recycle stream and are
30   separated, together with the condensed liquid, from the gaseous recycle stream in
the gas/liquid separator. Preferably, the fines are reintroduced into the fluidised bed
suspended in the liquid stream from the gas/liquid separator. Suitably, these
particles may be kept in suspension and thus avoid fouling of the gas/liquid
separator by, for example, stirring the liquid in the gas/liquid separator (mechanical
35   agitation), bubbling a gaseous stream through the liquid or continuously circulating

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the liquid by means of an external loop i.e. liquid is continuously withdrawn from and returned to the separator. Preferably, a portion of the liquid in the separator is continuously circulated by means of a pump. Suitably, sufficient liquid is circulated to allow the pump to be operated in a continuous manner. A portion of the

5   circulating liquid may be introduced directly into the fluidised bed via a valve which opens to allow liquid to enter a supply line to the fluidised bed. Preferably, the valve is operated via a liquid level controller which monitors and maintains the level of liquid in the separator between set limits.

The gaseous recycle stream may also comprise inert hydrocarbons used for

10   the injection of catalyst, reaction activators or moderators into the reactor.

Make-up monomers, for example, ethylene or propylene to replace monomers consumed by the polymerisation reaction may be added to the gaseous recycle stream at any suitable location.

Make-up condensable comonomers, for example, butene, hexene, 4-

15   methylpent-1-ene and octene, to replace condensable comonomers consumed by the polymerisation reaction may be introduced as liquids and added to the gaseous recycle gas stream at any suitable location.

Inert condensable liquids, for example, pentane may for example be injected into the gaseous recycle stream between the heat exchanger and the separator. For

20   the preparation of LLDPE, the comonomer, for example, but-1-ene can, if desired, be injected into the gaseous recycle stream before passage to the heat exchanger.

Suitable means for separating the liquid are for example cyclone separators, large vessels which reduce the velocity of the gas stream to effect separation (knock-out drums), demister type gas-liquid separators and liquid scrubbers, for

25   example, venturi scrubbers. Such separators are well known in the art.

The use of a demister type of gas-liquid separator is particularly advantageous in the process of the present invention.

A further advantage of using a demister type of separator is that the pressure drop within the separator can be lower than in other types of separators

30   thereby enhancing the efficiency of the overall process.

A particularly suitable demister separator for use in the process of the present invention is a commercially available vertical gas separator known as a "Peerless" (Type DPV P8X). This type of separator uses the coalescence of liquid droplets on a baffle arrangement to separate the liquid from the gas. A large liquid

35   reservoir is provided in the bottom of the separator for collection of the liquid and

into which the condensable liquid is charged before commencing cooling of the gaseous recycle stream to a temperature at which liquid condenses out. The liquid reservoir enables the liquid to be stored thereby providing control over the introduction of the liquid from the separator into the fluidised bed. This type of separator is very efficient and gives 100 % separation of condensed liquid from the gas stream. The separated liquid washes any fines from the baffle arrangement thus avoiding fouling of the baffles.

If desired, a filter mesh, or other suitable means, may be arranged in the liquid reservoir of the separator to collect any remaining fines present in the separated liquid.

The liquid from the separator together with any fines is suitably introduced into the fluidised bed above the upper limit of the temperature gradient between the entering fluidising gas and the remainder of the bed. The introduction of liquid from the separator may be at a plurality of points within this region of the fluidised bed and these may be at different heights within this region. The point or points of introduction of the liquid are arranged such that the local concentration of liquid does not adversely affect the fluidisation of the bed or the quality of the product, and to enable the liquid to disperse rapidly from each point and vaporise in the bed to remove the heat of polymerisation from the exothermic reaction. In this way the amount of liquid introduced for cooling purposes may much more closely approach the maximum loading that can be tolerated without disturbing the fluidisation characteristics of the bed and hence offers the opportunity to achieve enhanced levels of reactor productivity.

The liquid can, if desired, be introduced into the fluidised bed at different heights within the bed. Such a technique can facilitate improved control over comonomer incorporation. Controlled metering of liquid into the fluidised bed provides useful additional control over the temperature profile of the bed and, in the case that the liquid contains comonomer, provides useful control over the comonomer incorporation into the copolymer.

The liquid is preferably introduced into the lower part of the region of the fluidised bed above the upper limit of the temperature gradient between the entering fluidising gas and the remainder of the bed. Commercial processes for the gas fluidised bed polymerisation of olefins are generally operated under substantially isothermal, steady state conditions. However, although almost all of the fluidised bed is maintained at the desired substantially isothermal

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polymerisation temperature, there normally exists a temperature gradient in the region of the bed immediately above the point of introduction of the cooled gas stream into the bed. The lower temperature limit of this region wherein the temperature gradient exists is the temperature of the incoming cool gas stream, and the upper limit is the substantially isothermal bed temperature. In commercial reactors of the type which employ a fluidisation grid, typically 10-15 m high, this temperature gradient normally exists in a layer of about 15 to 30 cm (6 to 12 inches) above the grid.

In order to gain the maximum benefit of the cooling of the separated liquid it is important that the liquid injection means is arranged in the bed above the region where this temperature gradient exists. i.e. in the part of the bed which has substantially reached the temperature of the gaseous stream leaving the reactor.

The point or points of introduction of the liquid into the fluidised bed may for example be approximately 50-200 cm, preferably 50-70 cm above the fluidisation grid.

In practice, the temperature profile within the fluidised bed may first be determined during polymerisation using, for example, thermocouples located in or on the walls of the reactor. The point or points of introduction of the liquid is/are then arranged to ensure that the liquid enters into the region of the bed at which the returned gas stream has substantially reached the temperature of the gaseous recycle stream being withdrawn from the reactor.

It is important to ensure that the temperature within the fluidised bed is maintained at a level which is below the sintering temperature of the polyolefin constituting the bed.

The gas from the separator is recycled to the bed, normally into the bottom of the reactor. If a fluidisation grid is employed, such recycle is normally to the region below the grid, and the grid facilitates uniform distribution of the gas to fluidise the bed. The use of a fluidisation grid is preferred.

The process of the present invention is operated with a gas velocity in the fluidised bed which must be greater than or equal to that required to achieve a bubbling bed. The minimum gas velocity is generally approximately 6 cm/sec but the process of the present invention is preferably carried out using a gas velocity in the range 30 to 100, most preferably 50 to 70 cm/sec.

The catalyst or prepolymer can, if desired, be introduced into the fluidised bed directly with the separated liquid stream. This technique can lead to improved

dispersion of the catalyst or prepolymer in the bed.

If desired, liquid or liquid-soluble additives, for example, activators, cocatalysts and the like, can be introduced into the bed together with the liquid stream from the separator.

In the case that the process of the present invention is employed to make ethylene homo- or copolymers, make-up ethylene, for example, to replace the ethylene consumed during the polymerisation, may be advantageously introduced into the separated gas stream prior to its reintroduction into the bed (for example below the fluidisation grid if such is employed). By adding the make-up ethylene to the separated gas stream rather than into the gaseous recycle stream before separation, the quantity of liquid which may be recovered from the separator may be increased and the productivity improved.

The liquid stream from the separator may be subjected to additional cooling (e.g. using refrigeration techniques) before being introduced into the fluidised bed. Preferably, the liquid stream is subjected to additional cooling whilst being externally circulated, as described above, by including a cooler in the external loop. This allows an even greater cooling effect in the bed than is provided by the liquid evaporative effect (latent heat of evaporation) alone, thereby providing further potential increases in productivity of the process. Cooling of the liquid stream from the separator may be achieved by use of suitable cooling means e.g. a simple heat exchanger or refrigerator located between the separator and the reactor or between the point at which liquid is removed from and reintroduced to the separator. A further advantage of this particular aspect of the present invention is that, by cooling the liquid before introduction into the fluidised bed, any tendency for catalyst or prepolymer which may be contained in the liquid stream to cause polymerisation before introduction into the bed will be reduced.

The liquid may be introduced into the fluidised-bed by suitably arranged injection means. A single injection means may be used or a plurality of injection means may be arranged within the fluidised bed.

A preferred arrangement is to provide a plurality of injection means substantially equally spaced in the fluidised bed in the region of the introduction of the liquid. The number of injection means used is that number which is required to provide sufficient penetration and dispersion of liquid at each injection means to achieve good dispersion of liquid across the bed. A preferred number of injection means is four.

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Each of the injection means may, if desired, be supplied with liquid from the separator by means of a common conduit suitably arranged within the reactor. This can be provided, for example, by means of a conduit passing up through the centre of the reactor.

5   The injection means are preferably arranged such that they protrude substantially vertically into the fluidised bed, but may be arranged such that they protrude from the walls of the reactor in a substantially horizontal direction.

The rate at which liquid can be introduced into the bed depends primarily on the degree of cooling desired in the bed, and this in turn depends on the desired

10   rate of production from the bed. The rates of production obtainable from commercial fluidised bed polymerisation processes for the polymerisation of olefins depend, inter alia on the activity of the catalysts employed, and on the kinetics of such catalysts. Thus, for example, when catalysts having very high activity are employed, and high production rates are desired, the rate of liquid addition will be

15   high. Typical rates of liquid introduction may be, for example, in the range 0.25 to 4.9, preferably 0.3 to 4.9 cubic metres of liquid per cubic metre of bed material per hour, or even higher. For conventional Ziegler catalysts of the "superactive" type (i.e. those based on transition metal, magnesium halide and organometallic cocatalyst, the rate of liquid addition may be, for example, in the range 0.5 to 1.5

20   cubic metres of liquid per cubic metre of bed material per hour.

In the process of the present invention the weight ratio of liquid:total gas which may be introduced into the bed can be for example in the range 1:100 to 2:1, preferably in the range 5:100 to 85:100, most preferably in the range 6:100 to 25:100. By total gas is meant the gas which is returned to the reactor to fluidise

25   the bed together with any gas used to assist in the operation of the injection means, e.g. atomising gas. The atomising gas may suitably be an inert gas, for example, nitrogen but is preferably make-up ethylene.

By injecting the liquid into the fluidised bed in this way any catalyst which is present in the liquid may benefit from the localised cooling effect of the liquid

30   penetration surrounding each injection means which may avoid hot spots and consequent agglomeration.

Any suitable injection means may be used provided the penetration and dispersion of the liquid into the bed from such means is sufficient to achieve a good dispersion of liquid across the bed.

35   The preferred injection means is a nozzle or a plurality of nozzles which

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include gas-induced atomising nozzles in which a gas is used to assist in the
injection of the liquid, or liquid-only spray-type nozzles.

According to another aspect of the present invention there is provided a
start-up process of a continuous gas fluidised bed process for the polymerisation of
5   olefin monomer selected from (a) ethylene, (b) propylene, (c) mixtures of ethylene
and propylene, and (d) one or more other alpha-olefins mixed with (a), (b) or (c),
in a fluidised bed reactor by continuously recycling a gaseous stream comprising at
least some of the ethylene and/or propylene through a fluidised bed in said reactor
in the presence of a polymerisation catalyst under reactive conditions, cooling at
10   least part of said gaseous stream withdrawn from said reactor to a temperature at
which liquid condenses out, separating at least part of the condensed liquid from
the gaseous stream, and introducing at least part of the separated liquid directly
into the fluidised bed using one or more gas-induced atomising nozzles or one or
more liquid-only nozzles, characterised in that at least part of the gaseous recycle
15   stream by-passes the hereabove cooling/condensing/separating steps, and is
reintroduced as the recycling by-pass gaseous stream passing through the reactor.

The liquid injection means are suitably nozzles which protrude into the bed
through the reactor wall (or through a supporting grid for the bed) and which carry
one or more jet outlets to deliver the liquid to the bed.

20   It is important in the process of the present invention to achieve good
dispersion and penetration of the liquid in the bed. Factors which are important in
achieving good penetration and dispersion are the momentum and direction of the
liquid entering the bed, the number of points of introduction of the liquid per unit
cross-sectional area of the bed, and the spatial arrangement of the points of
25   introduction of the liquid.

The liquid from the separator may be introduced into the reactor as one or
more jets of liquid alone, or one or more jets of liquid and gas, from one or more
jet outlets, each jet having a horizontal momentum flux in the case of the liquid
only jets of at least 100×10^3 Kg s^{-1} m^{-2} x m s^{-1} and in the case of the gas/liquid
30   jets of 200 Kg s^{-1} m^{-2} x m s^{-1} wherein the horizontal momentum flux is defined as
the mass flow rate of liquid (kilogrammes per second) in the horizontal direction
per unit cross-sectional area (square metres) of the jet outlet from which it
emerges, multiplied by the horizontal component of the velocity (metres per
second) of the jet.

35   Preferably the momentum flux of each of the liquid or liquid/gas jets is at

least 250×10^3 and most preferably at least 300×10^3 Kg s^{-1} m^{-2} x m s^{-1}.
Particularly preferred is the use of a horizontal momentum flux in the range
300×10^3 to 500×10^3 Kg s^{-1} m^{-2} x m s^{-1}. In the case that the liquid jet emerges
from the jet outlet in a direction other than horizontal, the horizontal component of
the velocity of the jet is calculated from Cosine Q° x actual jet velocity, wherein Q°
is the angle the jet makes with the horizontal.

The direction of motion of the one or more liquid or liquid/gas jets into the
bed is preferably substantially horizontal. In the case that one or more of the jet
outlets deliver the liquid or liquid/gas jets in a direction other than horizontal,
preferably these are directed at an angle not greater than 45°, most preferably not
more than 20° to the horizontal.

Suitable gas-induced atomising nozzles and liquid-only nozzles are as
described in WO 94/28032, the contents of which are hereby incorporated by
reference.

Before commencing the introduction of liquid by use of the process
according to the present invention the gas phase fluidised bed polymerisation may
be started by charging the bed with particulate polymer particles, charging the
separator with liquid and then initiating the gas flow through the bed.

Processes according to the present invention will now be illustrated with
reference to the accompanying drawings.

Figures 1-3 show diagrammatically processes according to the present
invention.

Figure 1 illustrates a gas-phase fluidised bed reactor consisting essentially
of a reactor body 9 which is generally an upright cylinder having a fluidisation grid
10 located in its base. The reactor body comprises a fluidised bed 11 and a
velocity reduction zone 12 which is generally of increased cross-section compared
to the fluidised bed.

The gaseous reaction mixture leaving the top of the fluidised bed
reactor constitutes gaseous recycle stream and is passed via line 13 to a cyclone 14
for the separation of the majority of the fines. Removed fines may suitably be
returned to the fluidised bed. The gaseous recycle stream leaving the cyclone
passes to a first heat exchanger 15 and a compressor 16. A second heat exchanger
17 is present to remove the heat of compression after the gaseous recycle stream
has passed through the compressor 16 and also to cool the recycle stream to a
temperature such that a condensate is formed.

The heat exchanger or exchangers can be arranged either upstream or downstream of the compressor 16.

After compression and cooling to a temperature such that a condensate is formed, the resultant gas-liquid mixture is passed to the separator 18 where the
5   liquid is removed.

The gas leaving the separator is recycled via line 19 to the bottom of the reactor 9. The gas is passed via the fluidisation grid 10 to the bed thereby ensuring that the bed is maintained in a fluidised condition.

The separated liquid from the separator 18 is passed via line 20 to the
10   reactor 9. A pump 21 is suitably located in line 20.

Catalyst or prepolymer are fed to the reactor via line 22 into the separated liquid stream.

Product polymer particles are removed from the reactor via line 23.

As shown in Figure 1, part of the gaseous recycle stream by-passes the heat
15   exchanger 17 and the separator 18 by passing through line 24 ; said part of gaseous recycle stream is introduced in line 19 with the cold gaseous recycle stream and is recycled to the bottom of the reactor 9.

The arrangement shown in Figure 1 is particularly suitable for use when retrofitting existing gas phase polymerisation reactors using fluidised bed
20   processes.

Figure 1 also shows an optional additional heat exchanger 30 (in line 24). Said configuration including the additional heat exchanger represents a preferred embodiment of the present invention wherein the by-pass gas stream is cooled to a temperature above which liquid condenses out (or above the dew point) before its
25   reintroduction in the reactor.

Figure 2 illustrates an alternative arrangement for performing the process of the present invention. In this arrangement the compressor 16 is located in line 19 after separation of the gaseous recycle stream by the separator 18. This has the advantage that the compressor has a reduced quantity of gas to compress and can
30   therefore be of reduced size achieving a better process optimisation and cost.

Figure 3 illustrates a further arrangement for performing the process of the present invention whereby the compressor 16 is again arranged in line 19 after the separator 18 but before the second heat exchanger 17 which is located in the separated gas stream rather than located before the separator. Again this
35   arrangement gives a better process optimisation.

Claims

1.   Start-up process of a continuous gas fluidised bed process for the polymerisation of olefin monomer selected from (a) ethylene, (b) propylene, (c) mixtures of ethylene and propylene, and (d) one or more other alpha-olefins mixed with (a), (b) or (c), in a fluidised bed reactor by continuously recycling a gaseous
5   stream comprising at least some of the ethylene and/or propylene through a fluidised bed in said reactor in the presence of a polymerisation catalyst under reactive conditions, cooling at least part of said gaseous stream withdrawn from said reactor to a temperature at which liquid condenses out, separating at least part of the condensed liquid from the gaseous stream, and introducing at least part of
10   the separated liquid directly into the fluidised bed using a liquid injection means, characterised in that at least part of the gaseous recycle stream by-passes the hereabove cooling/condensing/separating steps, and is reintroduced as the recycling by-pass gaseous stream passing through the reactor.

2.   Continuous gas fluidised bed process for the polymerisation of olefin
15   monomer selected from (a) ethylene, (b) propylene, (c) mixtures of ethylene and propylene, and (d) one or more other alpha-olefins mixed with (a), (b) or (c), in a fluidised bed reactor by continuously recycling a gaseous stream comprising at least some of the ethylene and/or propylene through a fluidised bed in said reactor in the presence of a polymerisation catalyst under reactive conditions, cooling at
20   least part of said gaseous stream withdrawn from said reactor to a temperature at which liquid condenses out, separating at least part of the condensed liquid from the gaseous stream, and introducing at least part of the separated liquid directly into the fluidised bed using a liquid injection means, characterised in that at least part of the gaseous recycle stream by-passes the hereabove cooling/condensing/separating steps, and is reintroduced as the recycling
25   hereabove cooling/condensing/separating steps, and is reintroduced as the recycling

by-pass gaseous stream passing through the reactor.

3.   A process according to any one of claims 1 or 2 wherein the by-pass gas stream is reintroduced in the reactor below the bed together with the cold gaseous recycle stream coming from the separator.

5   4.   A process according to any one of claims 1 to 3 wherein the by-pass gas stream is cooled to a temperature above which liquid condenses out before reintroduction in the reactor.

5.   A process according to any one of claims 1 to 4 wherein   the liquid from the separator is introduced directly into the fluidised bed above the upper limit of

10   the temperature gradient between the entering fluidising gas (the gaseous stream fed to the reactor) and the remainder of the bed.

6.   A process according to any one of claims 1 to 5 wherein the one or more other alpha-olefins have from 4 to 8 carbon atoms.

7.   A process according to any one of claims 1 to 6 wherein the liquid injection

15   means is one or more gas-induced atomising nozzles or one or more liquid-only nozzles.
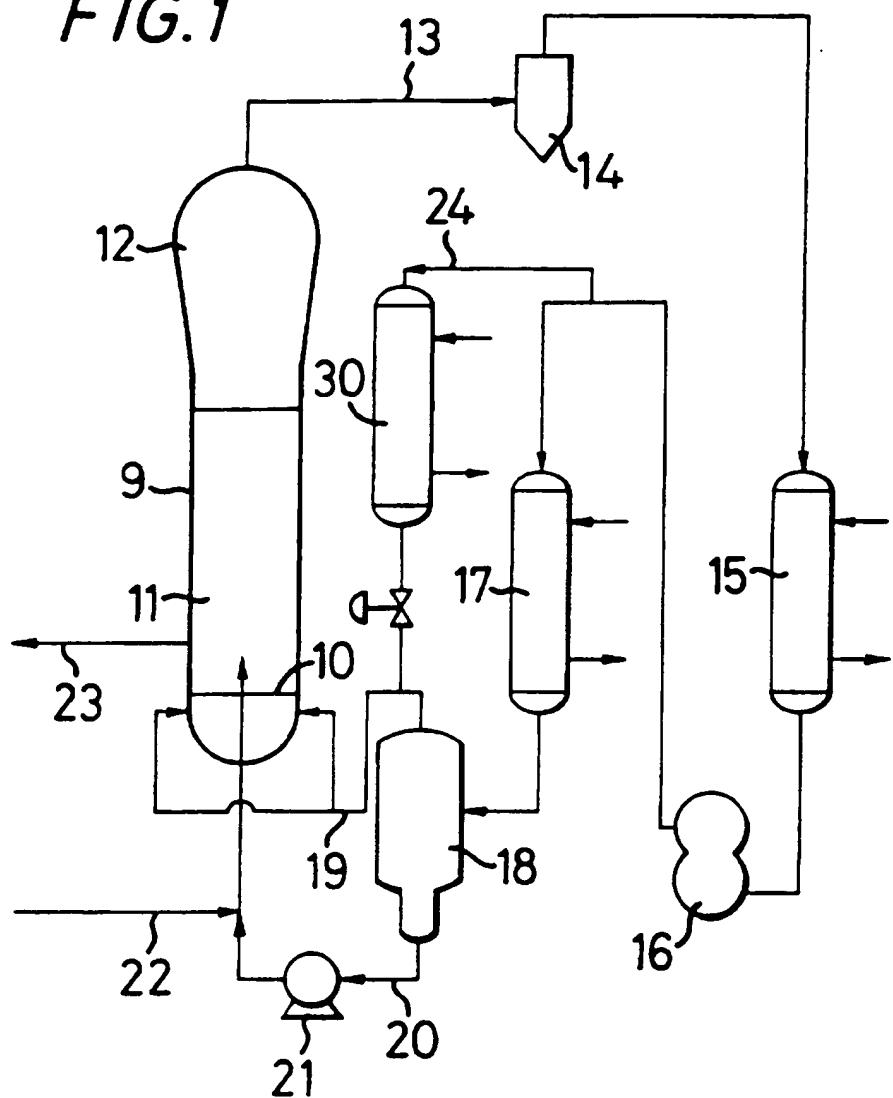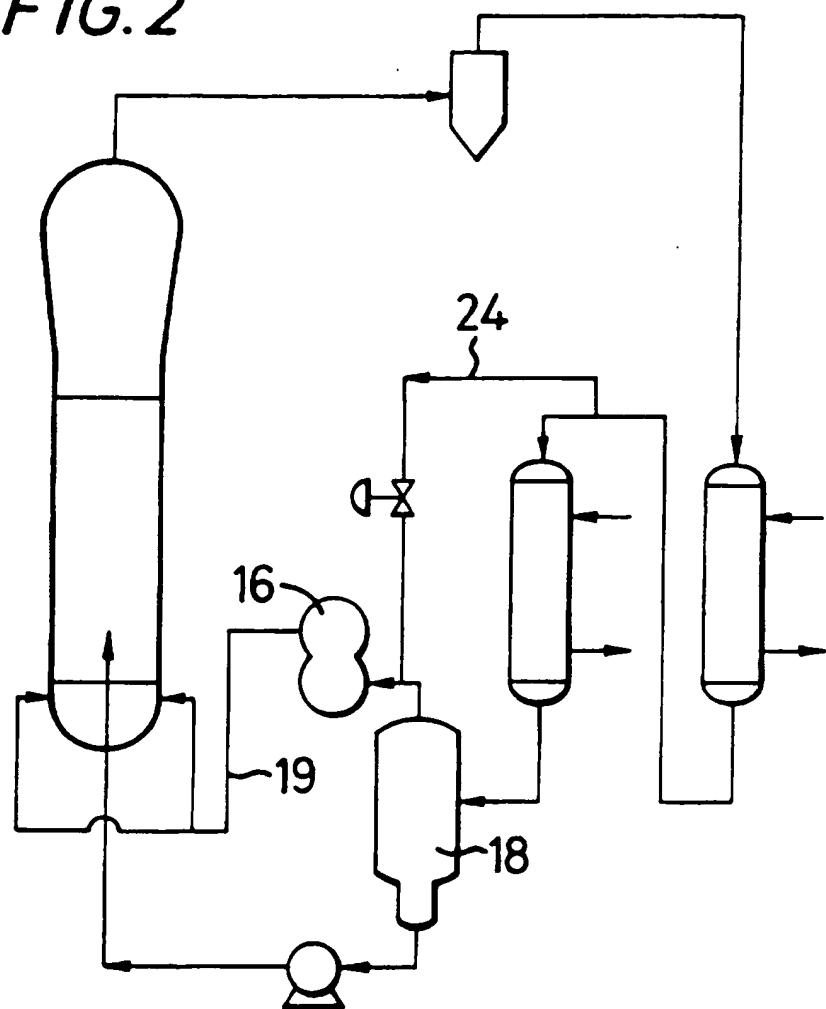
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FIG.1

FIG.2

FIG.3
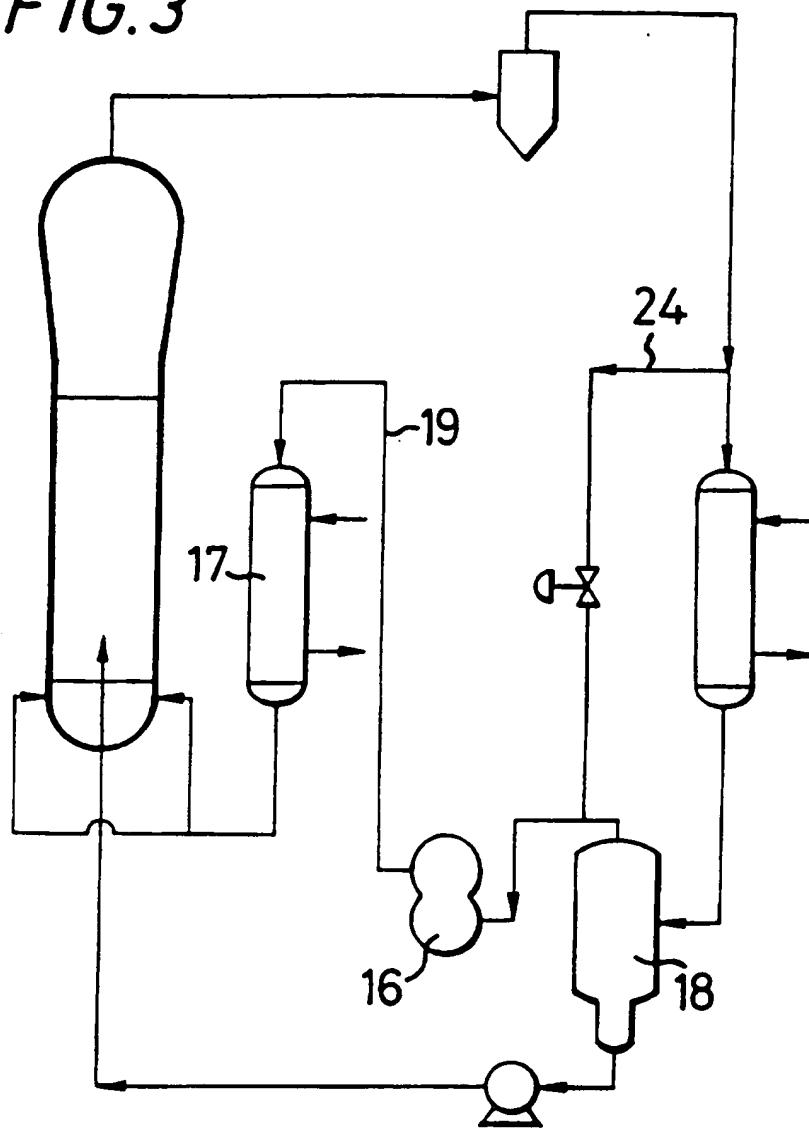
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6   C08F10/00   C08F2/34

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6   C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 94 28032 A (BP CHEMICALS LTD.) 8 December 1994 cited in the application see claims 1-6 see page 8, line 29 - page 9, line 7 see page 11, line 19 - line 22 ---	1-7
Y	US 5 376 742 A (KRAUSE STEPHEN) 27 December 1994 see claims 1-4 see column 3, line 47 - column 4, line 36 see column 5, line 34 - column 7, line 10 ---	1-7
A	EP 0 089 691 A (UNION CARBIDE) 28 September 1983 cited in the application see claims 1,18 --- -/--	1

[X] Further documents are listed in the continuation of box C.   [X] Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
11 April 1997	2 1. 04. 97

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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